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# Characterization of Ash From Tropical Biomass Gasification for Soil Fertilization

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**Abstract**
This study aims to determine the characteristics of bottom ash from the gasification of four agricultural biomasses namely corn stalks and cobs, cotton stalks, and wood residues, for potential use as agricultural fertilizer. The methodological approach consisted in carrying out gasification trials for each of these biomasses under identical operating conditions on a pilot-scale gasifier. The fly ash was collected at the end of the tests from the reactor bottom and cyclone bottom for analysis. Analysis showed that the ash from the reactor bottom contained higher levels of mineral elements, including Ca, P, K, and Mg in comparison to the cyclone bottom ash. However, the latter exhibited a higher content of Zn. Trace metallic elements (TMEs) were present in relatively low proportions. Ash from the gasification of cotton stalks had the highest Ca, Mg, K, and P content. The TME content was relatively above the required threshold, but it remained below the threshold in the ash from corn stalks. This suggests that cotton stalk ash is more suitable for use in agriculture as a soil fertilizer.

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## Introduction

Given the scarcity of fossil fuels and the negative impact of greenhouse gases on the environment, biomass has received increasing attention in recent years. It is potentially $CO_2$-neutral and renewable energy source.[1-2]

Waste-to-energy is highly favored due to the potential for cost savings in fuel transportation and the possibility of using biomass resources with minimal commercial value.[3] Biomass resources come in several forms: (i) waste from the plant kingdom/agricultural residues; (ii) waste from the

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animal kingdom; (iii) waste from agri-food structures; (iv) waste from aquatic sources; and (v) organic waste from communities and even industrial waste in addition to animal waste.[4]

Gasification technologies have developed rapidly and demonstrated their potential as a solution for the production of fuel gas and thermal energy in rural areas where agricultural waste (rice husks, groundnut hulls, cotton stalks, corn cobs, etc.) is abundant.[5-7]

In this context, Benin through the Government Action Plan (PAG 2016-2021: 45 Flagship Projects) has decided to invest in the field of renewable energies by focusing on the organization of the biomass-energy sector, in particular agricultural residues. The "Biomass Energy" project aims to install gasification power plants in four municipalities in the country, municipalities with abundant agricultural residues, for a total capacity of 15 MW.

Gasification equipment, some of which is commercially available in varying power ranges, can be used to convert biomass into electricity through cogeneration.[8]

During the thermochemical degradation of biomass, the non-combustible inorganic constituents of which it is composed remain in the form of ash residues. The ash content of woody waste is generally low, while it is relatively high in agricultural residues (case of rice husks: above 20%).

The growing consumption of biomass in energy applications is generating increasing quantities of ash. Its storage and disposal in landfill sites is costly and results in the loss of valuable resources.[10] It is important to recover these large quantities of ashes in connection with environmental protection; In doing so, jobs could be created.[4]

There are three main categories of use of ashes,[11-12-13] (1) Use as fuel in ovens; (2) Use in construction. Ashes can finally be used as a substitute for cement in concrete. However, it should be noted that most biomass-derived fly ashes cannot fulfill the specifications required for this application. (3) in the agricultural field: they are used as organic fertilizer (3) Use in agriculture: directly as organic fertilizer.

The ash essentially contains the following elements: Ca, Si, Al, Mg, Na, K, S, Fe, P and Mn. In this context, the ashes coming from the thermochemical valorization of agricultural biomass possess several types of nutrients: Mg, B, Ca and K etc.[14-15] Some of these elements (Zn, Fe, Cu, etc.) are classified as essential trace elements for plants, while others are essential for the metabolic pathways of photosynthesis. However, ashes contain heavy metals which negatively impact the quality of agricultural soils and the environment: this is also the case when they are infiltrated into groundwater and surface water.[16-17]

Since ashes do not have the same properties due to the nature of the biomass and the process leading to their generation, it is unlikely that these ashes will be valued in the same way.[9] According to Demirbas,[18] the composition of the ashes is closely linked to the nature of the plant species, the growing conditions and the nature of the processes. Before considering land application, ash from any biomass source must be carefully analyzed. Knowledge of the physicochemical properties of the ashes will make it possible to identify the appropriate type of recovery.[9] Particularly, there is a gap in the knowledge regarding the physicochemical properties of by-products derived from the gasification of different biomasses.

The present study aims to answer this concern through the performance of gasification tests on a pilot system with four (4) types of biomasses and comparative analyses of the chemical properties of their residual ashes in the laboratory.

## Materials and Methods

### Biomass Gasification Plant and Sampling of Ash

Located in the town of Porto-Novo in Benin, the co-current fixed bed gasifier, the subject of this study, was designed and manufactured in India by the company ONV BIO and the Indian Institute of Science (IISc) Bangalore (Figure 1). It is equipped with a gas mixture purification system, which includes a cyclone, two sprayers, a water purifier and a filter operating in series. (Figure 2). Due to the shape of the cyclone and the gas outlet pressure of the reactor, heavy particles in the gas fall by gravity and collect in the cyclone hopper. After several processing operations, the syngas are transported to the electric current generator.


**Fig. 1: Biomass gasification plant of Songhaï Center located in Porto-Novo, Benin**

The ash samples analyzed came from two locations: at the bottom of the gasifier reactor (S1) and at the cyclone separator (S2). These are depicted in Figure 2, which illustrates the gasification system.

Table 1 outlines the operational conditions associated with gasification and provides details regarding the sampling locations for ash.

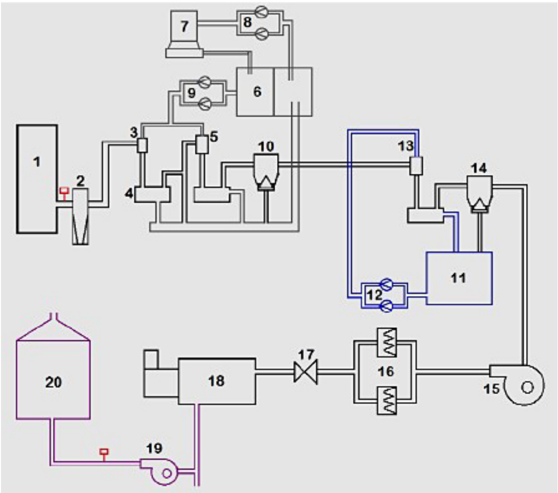


**Fig. 2: Gasification platform circuit**

| N° | Equipment Name | N° | Equipment Name |
|---|---|---|---|
| 1 | Reactor | 11 | Chiller |
| 2 | Cyclone | 12 | Chiller pumps |
| 3 | Water scrubber 1 | 13 | Chilled water scrubber |
| 4 | Gas liquid separation | 14 | Water trap 2 |
| 5 | Water scrubber 2 | 15 | Fan |
| 6 | Wash water tank | 16 | Bag filters |
| 7 | Cooling tower | 17 | Expansion valve |
| 8 | Cooling tower pumps | 18 | Motor |
| 9 | Water scrubber pumps | 19 | Exhaust gas fan |
| 10 | Water trap 1 20 Dryer | 20 | Dryer |

**Table 1: Experimental conditions**

| Operating conditions of gasification | Description |
|---|---|
| Biomass feeding rate | 20-35 kg. $h^{-1}$ |
| Gasification agent | Air |
| Reduction temperature | 700-800 °C |
| Ash sampling points | Temperature experience of gas phase around each point |
| Gasifier Reactor bottom $S_1$ | 400-600 °C |
| Cyclone bottom $S_2$ | 150-250 °C |

For each biomass, the tests were conducted in triplicate. Ash samples are taken during maintenance after the entire system has cooled down. Each sample taken is labeled, combining the code assigned to each biomass and the ash recovery point code (Figure 3).


**Fig. 3: Ash sample and labeled.**

Gasification feedstock and preparation for the tests
The raw materials used for the gasification tests in this study are corn stalks and cobs, cotton stalks, and *Acacia auriculiformis* wood (Figure 4).

The agricultural sector is a significant contributor to the national economy of Benin, accounting for 27% of the country's GDP in 2021. A study of ten agricultural seasons revealed that corn and cotton are the leading crops in terms of production,[19] which justifies the selection of these materials. For the 2017-2018 crop year, the quantities of maize and cotton residues produced are presented in Table 2.

**Table 2: Quantity of maize and cotton residues produced for the 2017-2018 crop year**

| Agricultural product | Waste or by -products | Quantity of product (ton) | Residues/ product ratio | Quantity of residues (ton) | Total (ton) |
|---|---|---|---|---|---|
| Maize | Cobs | 1 600 000 | 1 | 1 600 000 | 6 400 000 |
| | Stalks and leaf | | 3 | 4 800 000 | |
| Cotton | Stalks and cobs | 597 986 | 2,7 | 1 614 562 | 2 391 944 |
| | Shells | | 0,3 | 179 396 | |
| | Linter | | 1 | 597 986 | |

*Acacia auriculiformis* is a dedicated crop with high energy potential that is produced and used on the experimental site.

The physicochemical properties of the biomasses studied vary depending on whether it is the content of cellulose, hemicellulose, lignin, or the level of ash, volatile matter and fixed carbon.

Agricultural biomass was collected from fields in the commune of Parakou in northern Benin after harvest and transported to the gasification station. All samples underwent pre-treatment, which involved removing bulky leaves and branches.[20-21-22]

They were then cut into particles approximately 3cm x 3cm x 3cm in size and dried to achieve a humidity level below 15%. Drying was carried out using both open-air and solar drying methods (Figure 5). The humidity level was checked with a meter before each gasification test (Figure 6).

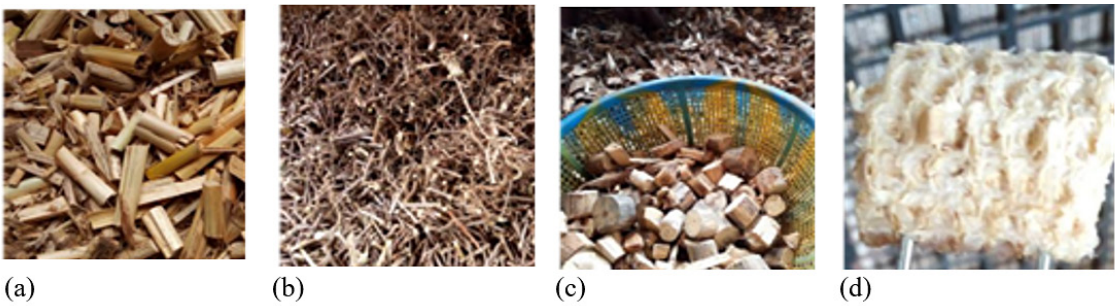

**Fig. 4: Feedstock used in this work, (a) Corn stalks, (b) Cotton stalks, (c) *Acacia auriculiformis* *Wood,* (d) Corn cobs**

**Fig. 5: Drying of feedstock: (a) Drying in a solar dryer, (b) Open-air drying**


**Fig. 6: Checking the moisture content**

**Ash Characterization Method**

The analyses were carried out at the Laboratory to Support the Improvement of Soil Health, Water Quality, and Environmental Protection (2A2S2E) of the Agricultural Research Institute of Benin (INRAB).

**Ash Content**

It is obtained by taking the ratio between the mass of ash obtained after incineration and the mass of the incinerated sample.

**Carbon Content**

The quantity of organic matter is determined by making the difference between the mass of the sample incinerated and the mass of the ashes obtained after incineration. The carbon content is determined by considering the empirical coefficient of 2 which assumes that the (quasi-crude) organic matter contains 50% carbon.[23]

**Silica and Metals Content**

The ash is dissolved in 5 cc of HCl, 6 N which is evaporated on a hot plate at 125 °C. The viscous residue obtained is recovered in 0.1 M $HNO_3$ and then filtered on ash-free paper in a 100 cc flask. The insoluble fraction is incinerated in the oven then reprocessed as before. The remainder recovered using the ashless paper is quantified and roughly corresponds to the siliceous fraction insoluble in acids. The solution thus obtained by successive filtrations is used to determine the metals by Atomic Absorption Spectrophotometry (AAS) or by Molecular Absorption Spectrophotometry (colorimetry). To minimize the effect of ionic interference during the absorption process, it is added to assay extracts of specific reagents. Thus, for the dosage of Ca and/or Mg, Lanthanum at 10 g $L^{-1}$ is used. For the dosage of sodium and/or potassium, the extracts are added with CsCl at 2 g $L^{-1}$.

**Total Phosphorus**

The extract obtained above is subjected to the hot action of ammonium molybdate and ascorbic acid. This action develops a blue-colored complex around P, which can be measured by colorimetry to determine the concentration of this metallic element.

**Results and Discussion**

The chemical analyses of the ash samples from *Acacia auriculiformis wood*, corn cobs, corn stalks, and cotton stalks have yielded the following results (Table 3). The values shown for each parameter are averages calculated from the data from the three trials carried out.

**Table 3: Nutrient and heavy metal concentrations in Gasifier Reactor and cyclone bottom ashes produced from four biomasses.**

| Elements | *Acacia auriculiformis* Wood | | Corn cobs | | Corn stalks | | Cotton stalks | |
|---|---|---|---|---|---|---|---|---|
| | $S_2^-$ cyclone bottom | $S_1^-$ Gasifier Reactor bottom | $S_2^-$ cyclone bottom | $S_1^-$ Gasifier Reactor bottom | $S_2^-$ cyclone bottom | $S_1^-$ Gasifier Reactor bottom | $S_2^-$ -cyclone bottom | $S_1^-$ Gasifier Reactor bottom |
| Si % | 3.33 | 9.67 | 3.59 | 11.37 | 3.53 | 11.47 | 3.95 | 4.39 |
| Ca % | 20.28 | 12.67 | 22.56 | 8.49 | 21.73 | 6.91 | 19.96 | 13.18 |
| Mg % | 1.25 | 1.46 | 1.19 | 0.97 | 1.21 | 1.36 | 1.19 | 2.12 |
| K % | 2.58 | 3.82 | 2.41 | 2.14 | 2.58 | 7.57 | 2.99 | 11.09 |
| Na % | 0.69 | 1.17 | 0.91 | 0.86 | 0.91 | 0.82 | 1.41 | 0.75 |
| P % | 0.82 | 1.21 | 0.61 | 0.73 | 0.69 | 2.15 | 0.57 | 2.16 |
| Fe % | 2.79 | 15.27 | 2.329 | 18.46 | 3.143 | 19.53 | 5.45 | 10.31 |
| Mn mg $kg^{-1}$ | 873.94 | 2004.23 | 1006.94 | 2408.54 | 1066.11 | 2532.25 | 1248.8 | 2232.77 |
| Cu mg $kg^{-1}$ | 114.21 | 155.71 | 103.56 | 237.89 | 116.84 | 123.12 | 113.15 | 227.46 |
| Zn mg $kg^{-1}$ | 3231.93 | 523.99 | 2158.73 | 507.92 | 2786.91 | 327.75 | 3996.29 | 286.61 |

Overall, ash from corn stalks is richer in Si, Fe, and Mn (microelements). Cotton stalk ash is richer in Ca, Mg, K, and Zn (macroelements and TMEs). Those from *Acacia auriculiformis* wood are richer in Na, P, and Cu. They reported that the composition of the ash depends on the nature of the woody biomass, the growth conditions and the nature of the process that led to the production of the ash.

We observe that the mineral element and heavy metal contents of the ashes collected at the cyclone level and at the reactor level are similar for corn stalks and ears. This composition is different from that presented by Adamon,[19] who instead carried out gasification of corn cob pyrolysis cokes. This result can be explained by the fact that the corn cobs would have lost some of their constituents during pyrolysis before being gasified and confirms that the ash content depends on the nature of the biomass used. The results obtained for *Acacia auriculiformis* wood ash corroborate those of Pan and Eberhardt,[3] who focused on the characterization of fly ash generated during the gasification of pine wood chips. They noted a high concentration in the order Ca-K-Mg-P for mineral matter and in the order Zn-Cu for TMEs. This suggests that wood in general is mainly rich in Ca and Zn.

It is also noted that with the exception of Ca, Na and Zn, the ashes collected in the reactor hopper contain higher levels of nutrients and Cu than those coming from the cyclone hopper. This could be justified by the presence of chemical components such as dolomite ($CaMg(CO_3)_2$) and limestone ($CaCO_3$), which are frequently used in gasification.

This would be the reason why ash from the cyclone hopper in our case is highly alkaline. In addition, volatile ash constituents such as Zn evaporate at high combustion chamber temperatures.[24-26]

Consequently, volatile constituents can be extracted from the heated ash bed and concentrated in the cyclone ash through condensation. There is an enhanced concentration of these elements in the cyclone ash compared to the bottom ash. This is also confirmed by Yao and *et al.*[5] who explain that during gasification, certain alkali metals in combination with other chemical elements present in the gasifier, cause partial condensation thus leading to retention of residual ashes in the form viscous. These results corroborate those of Bachmaier and *et al.*[27] who showed that Cu, and the main nutrients Mg, P, Ca, and K are less volatile and are therefore, predominantly remaining in the residual ash. For Li *et al.,*[28] gasification conditions play an important role in ash deposition. Indeed, Lanzerstorfer[25] observed that at combustor temperatures between 830 and 920 °C, Zn accumulates in the fly ash, while most nutrients (Ca, Mg) remain in the residual ash.

It is noted that the potassium contents in the bottom ash of all biomasses, except for corn cobs, are higher than those in the cyclone ash. Lanzerstorfer,[25] attributes the results to the high reaction temperatures, which are sufficient to remove volatile heavy metals while remaining below the threshold for high potassium losses. Bachmaier *et al.,*[27] found that if high concentrations of highly volatile elements are present in bottom ash intended for use as a fertilizer, increasing the temperature of the combustion bed may reduce these elements in the bottom ash and lead to an increase in cyclone ash.

The bottom ash analyzed in this study could therefore be used in the field of agriculture in the form of organic fertilizer.[3,9,29]

However, the composition of mineral substances is not sufficient to conclude. Another key point is the concentration of trace elements in the ash obtained. Based on the data available in the literature, Table 4 shows the maximum authorized thresholds of TMEs in biomass ash for soil application.

**Table 4: Maximum authorized limit for TMEs in biomass ash**

| Maximal concentration | Eco-SSL value from reference United States EPA 2003[3] | in Suisse from annex 2.6, ch. 2.2.1 of l'ORRChim (RS.814.81, 2011)[15] | In Royaume-Uni from ICRCL[30] |
|---|---|---|---|
| Cu (mg/kg) | 70 | 100 | 130 |
| Zn (mg/kg) | 160 | 400 | 300 |

Authorized limits vary from region to region. As the threshold values for Switzerland and the United Kingdom are close for both elements (Cu and Zn), we will use them for comparison with our results (Table 5).

Zn concentrations in the ash collected from the cyclone hopper are well above the threshold values of the two references (around 5 to 13 times). The ash is therefore less suitable for agricultural use. We will therefore focus the remainder of our analysis on the ash collected in the reactor hopper.

Comparison with the threshold values authorized in Switzerland shows that corn stalk ash and cotton stalk ash both comply with the 400 mg $kg^{-1}$ limit for Zn. However, the Cu concentration of cotton stalk ash is high compared with the threshold (100 mg $kg^{-1}$), whereas for corn stalk ash, it is relatively close to the threshold (123.122 mg $kg^{-1}$).

With the values presented for the United Kingdom, the Cu concentration in corn stalk ash complies with the threshold limit, as does the Zn concentration in cotton stalk ash. However, the Cu concentration in cotton stalk ash is well above the threshold, while the Zn concentration in corn stalk ash is slightly above the threshold.

From the above, it can be deduced that corn stalk ash recovered from the reactor hopper is more suitable for agricultural use.

**Table 5: Comparison of ETM concentrations with authorized limits**

| Elements | *Acacia auriculiformis* Wood | | Corn cobs | | Corn stalks | | Cotton stalks | | Limit in Suisse[15] | Limit in Royaume-Uni[30] |
|---|---|---|---|---|---|---|---|---|---|---|
| | $S_2^-$ cyclone bottom | $S_1^-$ Gasifier Reactor bottom | $S_2^-$ cyclone bottom | $S_1^-$ Gasifier Reactor bottom | $S_2^-$ cyclone bottom | $S_1^-$ Gasifier Reactor bottom | $S_2^-$ cyclone bottom | $S_1^-$ Gasifier Reactor bottom | | |
| Cu (mg kg$^{-1}$) | 114.21 | 155.71 | 103.56 | 237.89 | 116.84 | 123.12 | 113.15 | 227.46 | 100 | 130 |
| Zn (mg kg$^{-1}$) | 3231.93 | 523.99 | 2158.73 | 507.92 | 2786.91 | 327.75 | 3996.29 | 286.61 | 400 | 300 |

## Conclusion

This study analyzed the composition of gasification ash from four types of biomasses: corn stalks and cobs, cotton stalks, and wood residues, based on their mineral matter content, but especially their TME content, it emerged that only ash from maize stalks collected at the reactor hopper could be used in agriculture to fertilize soil. However, N should be added to boost the fertilizing effect. Similarly, appropriate dosing is required to dilute the ETM content and comply with the admissible limits.

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## Conflict of Interest

The author(s) declares no conflict of interest.

## Data Availability Statement

The manuscript incorporates all datasets produced or examined throughout this research study

## Ethics Statement

No experiments on humans or animals.

## Authors' Contribution

David Gildas Farid ADAMON and Charbel KINZO designed the study, performed the statistical analysis, and wrote the first draft of the manuscript. Djonoumawou Mèmèvêgni Grâce Floriane CHIDIKOFAN and Gloire AVIANSOU managed the literature searches and analyses of the study. All authors read and approved the final manuscript.

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